

## TESTING OF A SULFUR TOLERANT DIRECT METHANATION PROCESS

Allan Skov  
Haldor Topsoe, Inc.  
P. O. Box 58767  
Houston, Texas 77258

Karsten Pedersen  
Haldor Topsoe A/S  
P. O. Box 213, Nymollevvej 55  
DK-2800 Lyngby, Denmark

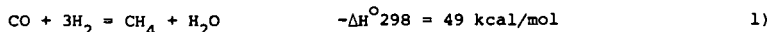
Chiang-liu Chen and Ralph L. Coates  
Questar Development Corporation  
141 East First South  
Salt Lake City, Utah 84147

### ABSTRACT

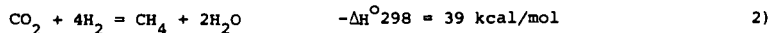
A new sulfur tolerant catalyst for methane formation from carbon monoxide and hydrogen has been tested at Haldor Topsoe's laboratory and at Mountain Fuel Resources' entrained coal gasification Process Development Unit. The catalyst also effectively catalyzes the shift reaction, which permits direct methanation of raw coal gas. In contrast to nickel-based methanation catalyst, it is not necessary to add steam for prevention of carbon formation. Physical and chemical properties of the catalyst have been characterized and reliable reaction rate expressions have been derived for optimization of the reactor design. Results of 1080 hours of testing time with raw gases produced from five different type coals showed no poisoning of the catalyst by impurities contained in the raw gas and no carbon formation on the catalyst surface. Near 100 percent conversion was achieved with respect to CO or  $H_2$ . Besides methane, the product gas also contained ethane and a small amount of propane.

### INTRODUCTION

Conventional methanation is normally carried out by reacting one molecule carbon monoxide with three molecules hydrogen to produce methane and steam:

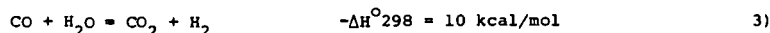


or one molecule carbon dioxide with four molecules of hydrogen to produce one molecule of methane and two molecules of steam:



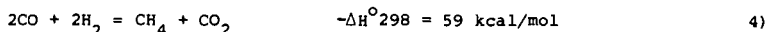
The reactions are catalyzed by various metals of which supported nickel is commonly employed (1).

The raw product gas from coal gasification typically contains higher concentrations of carbon monoxide than hydrogen, and the  $CO/H_2$  ratio ranges from 1 to 2 depending on the process. Therefore, in order to produce methane via reaction (1) above, the gas compositions have to be adjusted by the shift reaction:



and the excess  $CO_2$  has to be removed. Steam addition before methanation is required to prevent carbon formation on nickel catalysts and catalyst deactivation (2). Furthermore, since conventional catalysts are susceptible to sulfur poisoning, the hydrogen sulfide contained in the raw gas must be removed prior to methanation.

An alternate reaction for methane synthesis, which is known as direct methanation, is represented by the following reaction:



Haldor Topsoe, Inc., has recently developed a sulfur resistant catalyst for direct methanation as well as for the general reaction:



The main product of this reaction is methane. The hydrocarbons formed in addition to methane are saturated. Since the catalyst is activated by sulfur, the hydrogen sulfide contained in the raw feed gas has a positive effect on the reaction rate. The catalyst was first tested at Haldor Topsoe's laboratory in Denmark with synthetic gas simulating raw coal gas composition.

Besides being tolerant to sulfur, it is an effective catalyst for the shift reaction. Thus it offers the potential of greatly simplifying the coal to SNG process by eliminating the need for a shift reactor and sulfur removal upstream of the methanation reactor. Figure 1 presents a simplified block flow diagram to produce SNG from coal using sulfur tolerant direct methanation catalyst.

#### DESCRIPTION OF THE TEST UNIT

The methanation test unit was fabricated and partially assembled at the Haldor Topsoe Research Laboratory in Denmark and shipped to Mountain Fuel Resources (MFR) entrained coal gasification process development unit (PDU) in Utah. The unit was assembled and connected to the plant facility.

Figure 2 presents a simplified piping and instrument diagram of the unit. The unit consists of rotameters for hydrogen, hydrogen sulfide, nitrogen, and air, the methanation reactor, a fluidized sand bed for temperature control, heating elements, product gas condenser, product gas meter, temperature controller, temperature recorder, and other ancillary instruments.

The raw product gas slip stream from the gasifier was piped from the recycle gas surge tank to the reactor. The pressure was controlled by a pressure regulator upstream of the reactor and the flow rate was controlled by a needle valve downstream of the reactor. The temperature in the catalyst bed was measured with thermocouples placed inside thermowells centrally located along the length of the bed. The sand bath temperature was monitored with thermocouples embedded in the bath at several locations.

The catalyst has been tested previously in the Haldor Topsoe laboratory with synthetic raw gas in several experiments including a long-duration test of 1100 hours. This particular batch of catalyst installed at the PDU site, designated SMC 324, had been tested 440 hours at Haldor Topsoe's laboratory before it was shipped to the PDU.

#### EXPERIMENTAL

During the test, raw feed gas samples and product gas samples were taken periodically, approximately three to six times daily, and sent to Mountain Fuel Supply Company's gas laboratory for analysis. The samples were analyzed with a gas chromatograph for  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ , and  $\text{N}_2$ . The water vapor content of the product gas was measured by periodically weighing the condensate collected in the condenser.

The needle valve at the reactor exit was adjusted to obtain a desired gas flow rate. The space velocity was calculated based on the inlet gas flow. The conversion of carbon monoxide and hydrogen was calculated by:

$$X_{\text{CO}+\text{H}_2} = 1 - \frac{\text{Flow}_{\text{exit}} \cdot (\text{CO} + \text{H}_2)_{\text{exit}}}{\text{Flow}_{\text{in}} \cdot (\text{CO} + \text{H}_2)_{\text{in}}} \quad 6)$$

Direct sulfur resistant methanation testing was conducted at the MFR PDU for a cumulative total of 1080 hours between October 4 and November 21, 1984. Raw feed gases were produced from five different coals, Pittsburgh No. 8 eastern bituminous, North Dakota lignite, petroleum coke, Price River Utah bituminous and SUFPCO Utah bituminous.

During the tests conversion was kept at 90 percent in order to evaluate the catalyst activity. Occasionally, the  $\text{CO}/\text{H}_2$  ratio was adjusted with the addition of pure hydrogen into the feed. Hydrogen sulfide, in addition to that present in the feed gas from the coal, was added from time to time to study the effect of sulfur on the activity of the catalyst. Most of the tests were conducted at 300 psia pressure. When the pressure was varied to study the effect of pressure on the activity the feed flow to the reactor was reduced to attain the desired conversion.

## RESULTS

Table 2 presents the range of test conditions and test results and Figure 3 presents a plot of catalyst activity versus time. The activity was calculated as the space velocity for 90 percent conversion based on the rate limiting component; i.e., the minor component which is  $\text{H}_2$  for  $\text{CO}/\text{H}_2$  ratio of greater than 1.1 and CO for  $\text{CO}/\text{H}_2$  ratio of less than 1.1. Since the tests were conducted at different pressures and feed gas compositions, the space velocity to attain 90 percent conversion in pure  $\text{H}_2$  + CO at 300 psia total pressure was calculated to obtain a standard value of the catalyst activity.

Figure 3 also includes the activity of the catalyst during the tests at Haldor Topsoe with synthetic raw gas. The figure shows that the activity remained constant for the first 500 hours tested at the PDU. At this time a plant air compressor failure occurred which resulted in a temperature runaway of the methanator for more than 10 hours. Temperatures exceeded  $600^\circ\text{C}$ . After that the activity stabilized at a level of 0.87 times the initial value. The activity remained at this value throughout the rest of the test period despite two more temperature runaways at about 720 hours of operation.

The type of coal appeared to have no effect on the activity of the catalyst. The effect of variations in hydrogen sulfide concentration were also small. There appeared to be no effect of hydrogen sulfide on activity below 0.07 volume percent concentration. The catalyst activity remained constant during a 100 hour test with hydrogen sulfide partial pressure as low as 1 ppm.

## CONCLUSIONS

The direct, sulfur resistant methanation catalyst developed was successfully tested for 1080 hours at the MFR PDU with gases produced from five different type coals.

The catalyst was tested in several experiments with synthetic raw gas at the Haldor Topsoe laboratory in Denmark, including an 1100-hour continuous test. The particular batch sent to the PDU site had been tested for 440 hours in the laboratory.

Tests were conducted at 90 percent conversion level to evaluate catalyst activity at various test conditions. Near 100 percent conversion was achieved with respect to CO or  $\text{H}_2$ . The main hydrocarbon product was methane, which was produced in concentrations near 25 percent in the product gas. The product gas also contained ethane (about 2.5 percent) and propane (about 0.5 percent).

The activity was stable after more than 1500 hours of total operation. A slight drop in catalyst activity was observed after a temperature runaway above 600°C. This caused the activity to drop to 87 percent of the initial value. Two more temperature runaways thereafter had no effect on the activity.

The activity was not affected by the type of feedstocks to the gasifier. No poisoning of the catalyst by impurities contained in the raw feed gas was observed. The catalyst was examined after the tests and no carbon formation on the catalyst surface was observed.

The catalyst appears to be preferable to conventional methanation catalysts, especially in processing gas from coal gasification which contains high carbon monoxide.

The ethane and propane produced in addition to the methane provide a significant boost to the heating value of the product gas.

#### REFERENCES

- (1) "Catalytic Aspects of High Temperature Methanation," Pedersen, K., Skov, A., and Rostrup-Nielsen, J.R., Amer. Chem. Soc. Preprints Fuel Chemistry Division 25(2), March 1980, Houston, Texas
- (2) "Deactivation Phenomena of a Ni-based Catalyst for High Temperature Methanation," Gierlich, H. H., Fremery, M., Skov, A., Rostrup-Nielsen, J. R., pp. 459-469, Catalyst Deactivation, Elsevier, Amsterdam, 1980.

TABLE 1  
PHYSICAL CHARACTERISTICS OF THE CATALYST

Name	SMC 324
Size, L x D	4.5 mm x 4.5 mm (0.18" x 0.18")
Density	1.75 gm/cm <sup>3</sup> (109 lb/cf)
Bulk Density	1.275 Kg/l (80 lb/cf)
Surface Area	100 m <sup>2</sup> /gr
Crushing Strength	600 Kg/cm <sup>2</sup> (8700 lb/in <sup>2</sup> )

TABLE 2  
SUMMARY OF DIRECT METHANATION TEST CONDITIONS AND RESULTS

	Range of Test Conditions	Typical Test Data
Pressure, psia	90 - 300	300
Volumetric Flowrate, SCFH	1 - 8	3
Inlet Conditions (Adjusted with H <sub>2</sub> ), %		
CO/H <sub>2</sub> Ratio	0.7 - 1.5	1.0
H <sub>2</sub>	30 - 45	35
CO	30 - 45	40
CO <sub>2</sub>	10 - 40	15
H <sub>2</sub> S	1 ppm - 3.5	0.1
CH <sub>4</sub>	0 - 13	1
N <sub>2</sub>	2 - 11	5
Outlet Conditions, %		
H <sub>2</sub>	0 - 15	8
CO	2 - 15	8
CO <sub>2</sub>	40 - 55	50
H <sub>2</sub> S	2 ppm - 4.5	0.1
CH <sub>4</sub>	16 - 39	25
C <sub>2</sub> H <sub>6</sub>	1 - 4	2.5
C <sub>3</sub> H <sub>8</sub>	0.2 - 0.7	0.5
N <sub>2</sub>	Balance	Balance
Fractional Conversions		
CO	70 - 100	90
H <sub>2</sub>	70 - 100	90

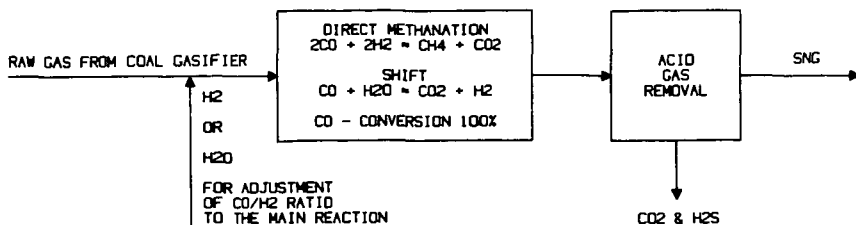


FIGURE 1. Block Flow Diagram, SNG from Coal by Direct Methanation Process

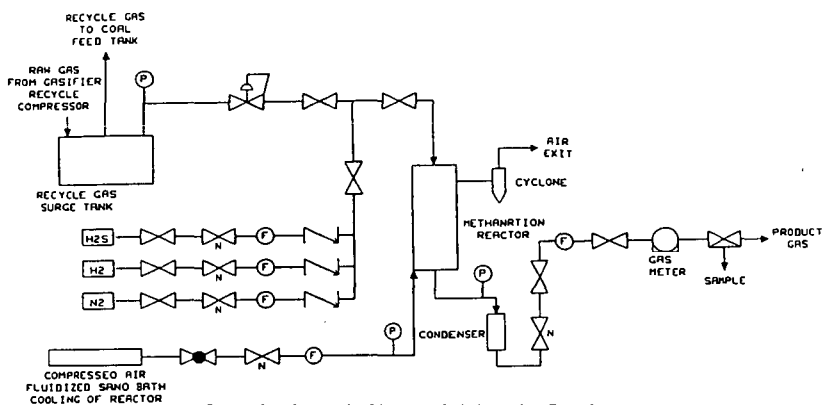


FIGURE 2. Schematic Diagram of Methanation Test System

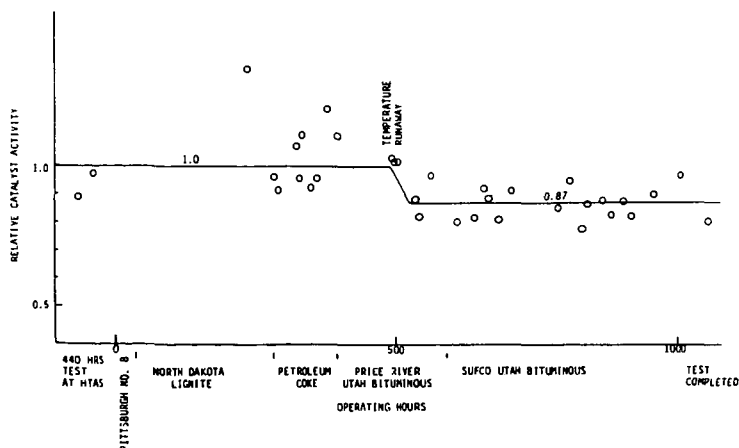


FIGURE 3. Relative Catalyst Activity Versus Time